

Electronic properties of the partially hydrogenated armchair carbon nanotubes

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By means of pseudopotential calculations based on density functional theory (DFT) we studied the effect of hydrogenation on electronic properties of armchair single-wall carbon nanotubes. The calculations demonstrate strong preference for formation of monoatomic H chains along the (5,5) nanotube axis with the H binding in an infinite H chain reaching the value of 2.58 eV per atom. Upon formation of chains of H adatoms, initially metallic (5,5) nanotubes change electronic structure to the semiconducting. The opening of the band gap of ~ 0.6 eV is accompanied with antiferromagnetic coupling of ferromagnetically ordered magnetic moments on C atoms in vicinity of the H chain. These electronic properties are strikingly similar to those previously observed in narrow graphene nanoribbons with zigzag edges.

I. INTRODUCTION

Graphene and graphene-based materials have attracted a great deal of interest due to their high stability and peculiar electronic properties,^{1–4} which make them suitable candidates for sensing applications,^{5,6} nanoelectronic components,^{7–9} or media for hydrogen storage.^{10–12} The most studied aspect of graphene is its electronic properties.³ At variance to conventional semiconductors, the electrons in graphene can move ballistically even at room temperature, which means the graphene can be used for design of electronic devices operating at the frequencies beyond the limits of the electronics based on silicon. However, being a zero-band-gap semiconductor graphene can not be used directly as a field-effect transistor for logic applications. Different strategies adopted in attempts to open a band gap in graphene include the substrate-induced band-gap,¹³ the use of bilayer graphene,^{14,15} graphene cutting into nanoribbons (GNR),^{16–19} or its hydrogenation.^{20–24} Only graphene hydrogenation and fabrication of GNR are methods able to open the band gap of 0.4 eV or more, as required for the applications in electronic devices operating at room temperature. However, hydrogen functionalization has been realized only on a conducting substrate, namely Ir(111).²³ This approach cannot be easily transferred to graphene on insulating substrates, which is needed for applications in electronics.

The GNRs have emerged as structures with great potential to become building blocks for carbon-based nanoelectronics after prediction to have band gaps useful for room temperature transistors, excellent switching characteristics, and ballistic transport properties.^{7,8,17} At variance to carbon nanotubes (CNTs) which exhibit extreme chirality dependence of metallic or semiconducting nature, the GNRs with the width below 10 nm are all semiconductors.^{16,18} Yet, producing narrow GNRs with high quality edges in order to preserve high-electron mobility of graphene remains a big challenge for state-of-the-art lithographic, chemical, or sonochemical methods. Recently, Jiao *et al.*²⁵ developed a new route

toward fabrication of the GNRs with smooth edges, starting from CNTs with narrow diameter and chiral distribution. Since the methods for synthesis and size control of the CNTs are well established, Jiao and co-workers based the fabrication of high-quality GNRs on unzipping of carbon nanotubes. The difficult task of cleaving CNTs along the axis was achieved by an Ar plasma etching method. The GNRs with smooth edges and width in range from 10 to 20 nm were produced. Further improvements of the method were realized through the mechanical sonification of mildly oxidized multiwall carbon nanotubes.²⁶

The decoration of graphene with H monoatomic lines was recently proposed in the computational studies of Chernozatonskii *et al.*^{27,28} as a new method to modify the electronic structure of graphene. The authors demonstrated that periodic H lines divide graphene into electronically independent strips which show electronic properties close to those of GNRs with armchair edges. Yet, the method proposed for the fabrication of these structures on graphene is questionable. Miller *et al.*²⁹ combined experimental observations with computational methods to investigate the hydrogenation of CNTs using high boiling polymers as hydrogenation reagents. The measured values of the C-H stretching vibrations are in good agreement with the those obtained for CNTs hydrogenated with H plasma.³⁰ According to the first-principles calculations reported in Ref.²⁹ the chemisorbed hydrogens should preferentially form axially aligned chains.

In the present work we focus on the electronic structure of hydrogenated CNTs and provide clear evidence that the electronic properties of metallic armchair CNTs can be tuned to those of semiconducting GNRs through adsorption of H atoms, without need for unzipping of CNTs. Our *ab-initio* calculations reveal that partial hydrogenation of CNTs leads to the formation of H chains along the tube axis, the structures which are thermodynamically favorable and kinetically stable at room temperature. We demonstrate that the CNTs decorated with H chains are magnetic semiconductors with electronic properties remarkably similar to those of

GNRs with zigzag edges. These results would contribute to development of experimental methods in band-gap engineering of carbon nanostructures based on their hydrogenation rather than high precision cutting of graphene or carbon nanotubes.

II. COMPUTATIONAL METHODS

The DFT calculations were performed with the plane-wave-based DACAPO program package,^{31,32} applying ultra soft pseudopotentials^{33,34} to describe electron-ion interactions, and the Perdew-Wang functional (PW91)³⁵ for the electronic exchange correlation effects. The electron wave functions and augmented electron density were expanded in plane waves with cutoff energies of 25 Ry and 140 Ry, respectively. In our investigation of the H interaction with metallic single-wall carbon nanotubes (CNTs) we have chosen the (5,5) nanotubes, since this class of extensively studied nanotubes offers the possibility to perform required calculations at modest computational cost. The calculations were performed using a supercell with dimensions of 19 Å in directions perpendicular to the nanotube axis and 9.84 Å along the axis. The Monkhorst-Pack scheme³⁶ with sixteen points was applied for sampling of the Brillouin zone. The activation energies related to the H diffusion on the CNT(5,5) were calculated using the nudged elastic band method.³⁷ In order to demonstrate that the main results of the study are applicable to other metallic nanotubes we performed a limited number of calculations for the (8,8) and (10,10) CNTs. All H binding energies are given relative to the energy of the free H atom.

Since the electronic and magnetic properties of nanostructures are often sensitive to the choice of pseudopotentials and their implementation we performed a set of additional calculations with the Quantum Espresso (QE) package.³⁸ The tests demonstrated that the results obtained with the DACAPO and QE codes are in very good agreement. The H binding energies at CNT(5,5) differ less than 0.03 eV per atom; the calculated band-gaps for H wire on CNT(5,5) [Fig.1d] are 0.58 eV (DACAPO) and 0.53 eV (QE). The local magnetic moments as well as local electronic properties are nearly identical. Hence, in the rest of the paper we present and discuss only results produced with the DACAPO code.

III. RESULTS AND DISCUSSION

A. Structural properties of partially hydrogenated armchair CNTs

The initial step in our investigation of the CNT(5,5) hydrogenation was the search for the thermodynamically most favorable structures formed by deposited H atoms. Starting with H monomers we calculated a binding

energy of 1.67 eV, which is considerably higher than the value of 0.8 eV obtained for graphene, applying the same computational approach.³⁹ The H dimers are the smallest H clusters on graphene stable at room temperature.⁴⁰ Several recent studies identified the ortho- (O) and para-dimers (P) as the most favorable dimer structures with similar H binding energies.^{39–41} The dimer adsorption picture on CNT(5,5) is more complicated than on graphene due to axial symmetry of the nanotube which leads to different types of the O and P dimers. The most stable dimer configuration on CNT(5,5) identified from our calculations are shown in Fig. 1(a). Thermodynamically preferential are tilted O

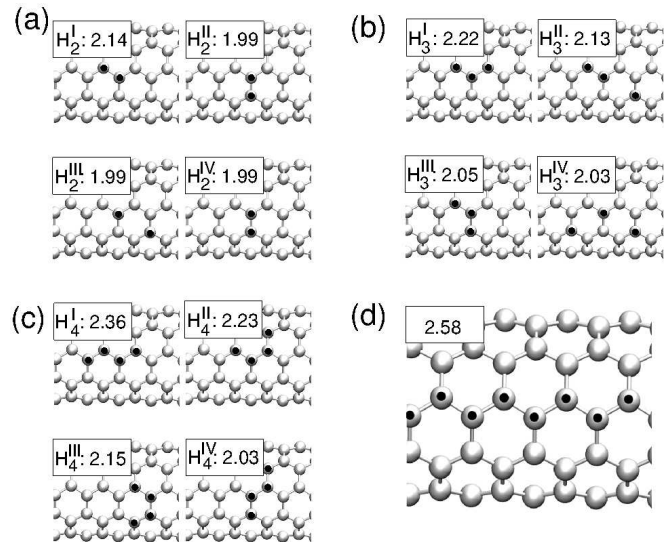


FIG. 1: The configurations of (a) dimers, (b) trimers, (c) tetramers, and (d) an infinite chain of H adatoms on CNT(5,5). The corresponding binding energies per H atom are in eV. H and C atoms are represented with small black and gray spheres, respectively.

dimers (configuration H_2^I), with binding energy of 4.28 eV, 0.94 eV more than binding of two isolated H atoms. This high binding energy confirms the strong tendency for clustering of H adatoms on carbon nanotubes, in agreement with expectation based on results produced for H adsorption on graphene.³⁹ Other favorable dimer structures depicted in Fig. 1(a) are 0.3 eV higher in energy than tilted O dimers.

According to our previous study⁴² the most stable configurations of H clusters with n adatoms ($2 \leq n \leq 6$) on graphene are exclusively composed of O and P dimers. The test calculations performed for H dimers and trimers on CNT(5,5) show that the same effect is found on armchair carbon nanotubes. This significantly reduces the number of H configurations which should be included in the search for the most stable H structures. Therefore, in the following we consider only H configurations in which all neighboring H atoms were configured as in O or P dimers.

The calculations performed for H trimers provide evi-

dence for tendency of H adatoms to cluster into chains oriented along the tube axis [see Fig. 1(b)]. The axially aligned H_3^I structure is 0.24 eV more favorable than the H_3^{II} trimer. The other two trimers in Fig. 1(b) are 0.51 eV (H_3^{III}) and 0.57 eV (H_3^{IV}) higher in energy than the H_3^I cluster.

Four tetramers considered in our study are presented in Fig. 1(c). The chain of H adatoms along the tube axis (H_4^I) is 0.5 eV more stable than the H_4^{II} structures. The third structure (H_4^{III}) is less stable by an additional 0.34 eV. The H_4^{IV} cluster oriented perpendicular to the tube axis is as much as 1.32 eV less stable than the H_4^I configuration, which further confirms the strong preference of H adatoms to align along the nanotube axis.

An infinite chain of H atoms along the tube axis, de-

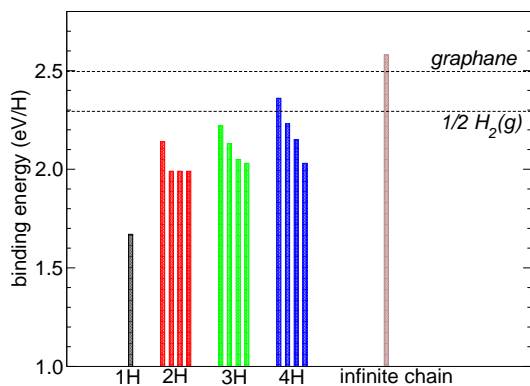


FIG. 2: Evolution of the H binding energy with the size of the configurations in Fig. 1. The calculated values are compared to those obtained in $H_2(g)$ and graphane.

picted in Fig. 1(d), is the particularly stable adsorption configuration. In the rest of the text we refer to this structure as the H-CNT(5,5). The calculated H binding energy is 2.58 eV per atom, considerably more than the 2.29 eV/H calculated for the gas-phase H_2 molecule or the 2.49 eV/H obtained for graphane. The chain of H adatoms was previously reported as a favorable configuration of H adatoms in a study of debundling and dispersing of CNTs upon their hydrogenation.²⁹ The H binding energies of all structures presented in Fig. 1 are compared in Fig. 2. In addition to the observed preference for axially aligned H chains, the plot clearly demonstrates an enhancement in thermodynamic stability of the chains with increase in their size.

We conclude our description of the structural properties of H chains on CNT(5,5) by examining their kinetic stability against H diffusion to the nearest C atoms, in the direction perpendicular to the nanotube axis. The calculated activation energy of 1.7 eV confirms that chains of H atoms aligned along the tube axis are kinetically highly stable at room temperature.

B. Electronic properties of partially hydrogenated armchair CNTs

Once the favorable structure of H adsorbates on the carbon nanotube is identified we focus on the electronic properties of the CNT(5,5) decorated with the chain of H adatoms. It turns out that the adsorbates profoundly change the electronic structure of the CNT(5,5), transforming it from a metal to a magnetic semiconductor. The π -bonding network of electronic bands in the vicinity of the Fermi level which originates from the $2p_z$ states of individual C atoms can be disrupted through hydrogen adsorption, since the contribution from the C $2p_z$ orbitals of hydrogenated C atoms is removed from the π bonds near the Fermi level upon their hybridization with H 1s orbitals. Hence, instead of cutting graphene into ribbons, the edges at the π -bonding network of the C- $2p_z$ states can be produced with chains of adsorbed H atoms. The zigzag chain of H adatoms breaks the cyclic boundary conditions of pristine CNT(5,5), creating open boundary conditions similar to those in zigzag carbon nanoribbons (ZGNRs). Thus, the electronic structure of CNT(5,5) with the H line is expected to show considerable similarity to the electronic structure of ZGNRs. We now illustrate the striking similarity of the valence and conduction bands in GNRs and hydrogenated CNT(5,5) by comparison of their main features:

(i) The calculated band gap in H-CNT(5,5) is 0.58 eV.

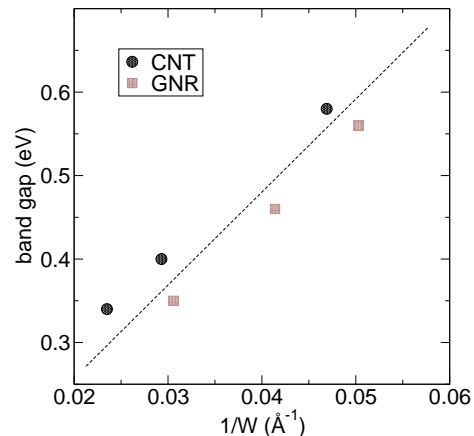


FIG. 3: Evolution of the band-gap size of partially hydrogenated CNTs and ZGNRs with their width (W). We assume that the widths of CNTs are identical to their circumferences.

Our calculations for bigger nanotubes indicate decrease of the band-gap size with the nanotube diameter. For H-CNT(8,8) and H-CNT(10,10) we calculated values of 0.40 and 0.34 eV, respectively. The trends in the band gaps of the H-CNTs are fully in line with those observed for ZGNRs,^{16,18} as demonstrated in Fig. 3, where we presented results for partially hydrogenated CNT(n,n) ($n=5,8,10$), as well as for m-ZGNRs ($m=8,10,16$), chosen as the nanostructures with widths comparable to those of the CNTs considered here.⁴³

(ii) The band-gap opening in H-CNTs and ZGNRs is driven by the same physical mechanism, i.e. the exchange interaction. To demonstrate this finding we performed non-spin-polarized calculations for two considered types of nanostructures. The corresponding total densities of states (DOS) are depicted in Fig. 4. For both systems,

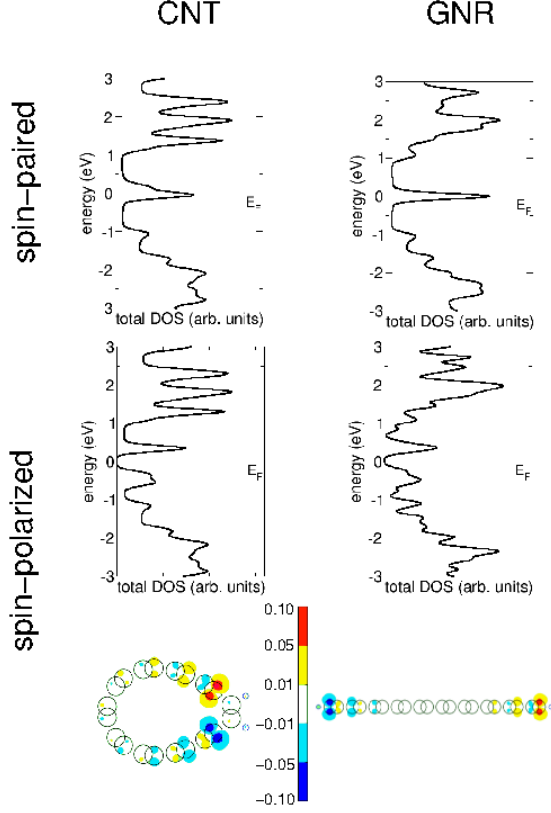


FIG. 4: Total density of states (DOS) of CNT(5,5) decorated with H chain and 10-ZGNR, produced from spin-paired (top panels) and spin-polarized calculations (middle panels), as well as the corresponding spin densities (lowest panel) averaged along the nanotube or nanoribbon axis.

the H-CNT(5,5) and 10-ZGNR, very high values of DOS at E_F are obtained in spin-paired calculations. The corresponding electronic states are removed from the Fermi level when the on-site exchange interaction is switched on, which results in induced magnetic moments on C atoms, as well as in the band-gap opening. This mechanism of the band-gap opening in graphene-based nanostructures was already reported by Son *et al.* in their study of ZGNRs.¹⁶ The magnetic moments at C atoms belonging to the same zigzag chain along the tube or nanoribbon are ferromagnetically coupled, with different signs of magnetic moments for C atoms located on different sides of the H chain or near different zigzag edges. The spin density rapidly decays with the distance from the H chain or zigzag edge. Its main features are very similar for H-CNT(5,5) and 10-ZGNR (see lowest panel in Fig. 4).

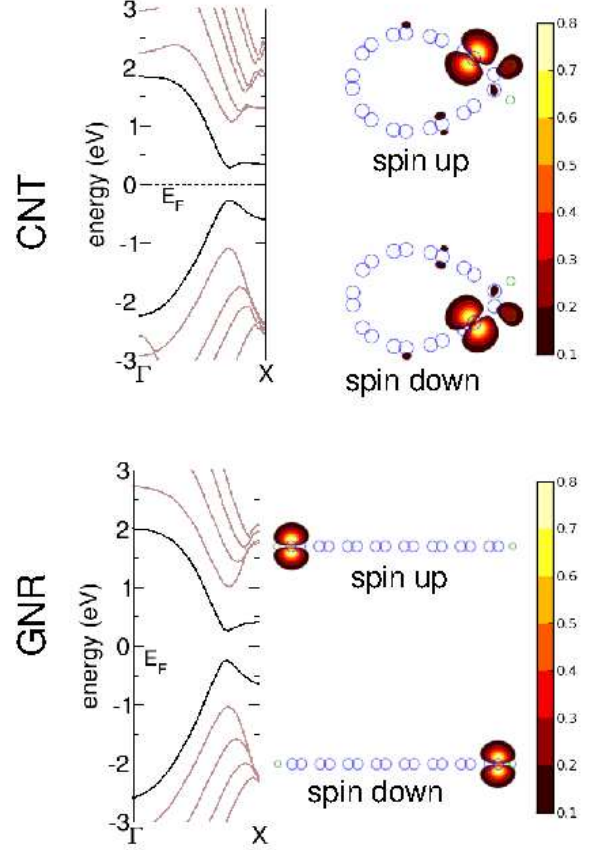


FIG. 5: Band structure diagrams (left) and the absolute value of the Kohn-Sham states (right) of CNT(5,5) decorated with H chain and of 10-ZGNR. The Kohn-Sham states of valence bands at X point are plotted in the planes perpendicular to the tube axis or nanoribbon edges. The H and C atoms are shown as small and big circles, respectively.

(iii) According to the tight-binding theory of ZGNRs^{44,45} very high values of the DOS at Fermi level are due to flat bands of the edge states. They are split due to exchange interaction and pushed below (valence band) and above (conduction band) E_F . These states decay with the distance from the edge with the decay profile depending on the momentum: The highest localization at the edges is observed at the X-point.^{46,47} The same type of edge states is also found in our study of the H-CNT(5,5). The edge states of H-CNT(5,5) and 10-ZGNR are compared in Fig. 5, where we presented isocontour plots of the absolute values of the Kohn-Sham states of the valence band at the X-point, for both spin orientations. The states corresponding to two different spin channels are located at different sides of the H chain [H-CNT(5,5)] or near different zigzag edges [GNRs]. The spin polarization of the edge states induces considerable magnetic moments on C atoms in the vicinity of the H lines (CNTs) or zigzag edges (GNR). The characters of these states in H-CNT(5,5) and 10-ZGNR (see Fig. 5)

are remarkably similar.

IV. CONCLUSIONS

Our thorough inspection of the electronic properties of armchair CNTs decorated with the chain of adsorbed H atoms demonstrates marked similarity between their electronic properties and those observed in ZGNRs. This similarity originates from the breaking of cyclic boundary conditions of pristine nanotubes upon H deposition, which leads to the creation of the edge states near the H chain, equivalent to the states observed at the edges of ZGNRs. Given the strong preference of H adatoms to assemble into chains oriented along the nanotube axis, together with the high kinetic stability of the formed structures, the partial hydrogenation of carbon nanotubes is a promising route for designing new nanostructures with electronic properties resembling those of narrow graphene nanoribbons. Our study

indicates that the hydrogenation opens prospects for achieving electronic properties of narrow GNRs without utilization of the challenging techniques of cutting graphene sheets or unzipping carbon nanotubes with (sub)nanometric precision.

The comparison of the electronic structure of partially hydrogenated CNTs and GNRs should be extended to the study of the hydrogenation of zigzag CNTs which are expected to obey electronic properties similar to those of armchair GNRs.

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